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## PATENT ABSTRACTS OF JAPAN

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YAMADA ATSUO(54) SYNTHESIS OF  $\text{LiFePO}_4$  AND MANUFACTURE OF NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enable synthesis at a low temperature without generating acid gas, and to realize high capacity by using at least iron oxalate as a synthetic raw material in a mixing process.

SOLUTION: Iron oxalate is used as a Fe source in a synthetic raw material of  $\text{LiFePO}_4$  used as a positive electrode active material. The iron oxalate can quickly advance synthetic reaction since a decomposition temperature is low, and does not damage a reaction device since acid gas is not generated at reaction. As the synthetic raw material, for example, the iron oxalate, ammonium hydrogenphosphate and lithium carbonate are mixed in the prescribed ratio to form a synthetic precursor. The  $\text{LiFePO}_4$  is synthesized by heating the precursor in an inert gas atmosphere. A synthetic temperature is desirably set to a range of 350°C to 790°C. Air included in the precursor is desirably removed by applying deaerating processing before heating/synthesizing the precursor.

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CLAIMS

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[Claim(s)]

[Claim 1] The synthetic technique of  $\text{LiFePO}_4$  which faces compounding  $\text{LiFePO}_4$ , has the mixed process which mixes two or more matter used as a synthetic powder, and is used as a precursor, and the heating process to which heat the above-mentioned precursor obtained at the above-mentioned mixed process, and it is made to react, and is characterized by using a ferrous oxalate at least as the above-mentioned synthetic powder in the above-mentioned mixed process.

[Claim 2] The synthetic technique of  $\text{LiFePO}_4$  according to claim 1 characterized by having the deaeration process which removes the gas contained in the above-mentioned precursor obtained at the above-mentioned mixed process between the above-mentioned mixed process and the above-mentioned heating process.

[Claim 3] The positive electrode which has for a lithium  $\text{LiFePO}_4$  in which a dope and a \*\* dope are possible in reversible as a positive active material, In the manufacture technique of the nonaqueous electrolyte cell equipped with the nonaqueous electrolyte which counters with the above-mentioned positive electrode, is allotted, and intervenes a lithium between the negative electrode which has the negative-electrode active material in which a dope and a \*\* dope are possible in reversible, and the above-mentioned positive electrode and the above-mentioned negative electrode Face compounding the above  $\text{LiFePO}_4$ , have the mixed process which mixes two or more matter used as a synthetic powder, and is used as a precursor, and the heating process to which heat the above-mentioned precursor obtained at the above-mentioned mixed process, and it is made to react, and it sets at the above-mentioned mixed process. The manufacture technique of the nonaqueous electrolyte cell characterized by using a ferrous oxalate at least as the above-mentioned synthetic powder.

[Claim 4] The manufacture technique of the nonaqueous electrolyte cell according to claim 3 characterized by having the deaeration process which removes the gas contained in the above-mentioned precursor obtained at the above-mentioned mixed process between the above-mentioned mixed process and the above-mentioned heating process.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture technique of a nonaqueous electrolyte cell of having used the synthetic technique of  $\text{LiFePO}_4$ , and its  $\text{LiFePO}_4$  as a positive active material.

[0002]

[Description of the Prior Art] In recent years, the research of the rechargeable battery in which a recharge is possible is advanced as a cell which can be used a long time, conveniently, and economically with fast progress of various electronic equipment. As a typical rechargeable battery, the lead accumulator, the alkaline battery, the lithium secondary battery, etc. are known.

[0003] Especially the lithium secondary battery has advantages, such as high power and a high-energy density, also in the above rechargeable batteries. A lithium secondary battery consists of the positive electrode and negative electrode which have the active material in which \*\*\*\*\* is possible in reversible, and nonaqueous electrolyte in a lithium ion.

[0004] Now,  $\text{LiCoO}_2$  is widely put in practical use as a positive active material which has the potential of 4V with the potential for a lithium. This  $\text{LiCoO}_2$  has a high-energy density and a high voltage, and is a positive-electrode material ideal in respect of being various.

[0005]

[Problem(s) to be Solved by the Invention] However, Co is unevenly distributed on an earth, and since it is rare resources, a cost attaches it highly, and also adequate supply carries out in difficulty, is in it, and it has flume \*\*\*\*\*. Therefore, instead of Co, it exists abundantly as resources and the development of the positive-electrode material which used cheap Mn as the base is desired.

[0006] As a positive-electrode material which used Mn as the base, it has normal-spinel type structure and  $\text{LiMn}_2\text{O}_4$  which has space group  $Fd3m$  is proposed. This  $\text{LiMn}_2\text{O}_4$  has high potential equivalent to  $\text{LiCoO}_2$  called 4V class with the potential for a lithium. Furthermore, from that synthesis is easy and having a high cell capacity,  $\text{LiMn}_2\text{O}_4$  is a very promising material, and is put in practical use.

[0007] However, by the cell actually constituted using  $\text{LiMn}_2\text{O}_4$ , the problem that that the capacity degradation at the time of an elevated-temperature store is large and Mn will melt into the electrolytic solution and that neither a stability nor a cycle property is enough is left behind.

[0008] On the other hand, various studies are made also about the positive-electrode material which used Fe as the base. Fe is a material abundant in resources, and cheaper than Mn, and if it can realize the positive-electrode material which used Fe as the base, it is still desirable.

[0009] As a positive-electrode material which used Fe as the base, although the study of the material which considers  $\text{LiFeO}_2$  which has structure similar to  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  as basic composition is carried out to the center,  $\text{LiFeO}_2$  has unstable structure to the top where production is difficult, and sufficient property is not realized as a positive active material for rechargeable batteries.

[0010] On the other hand, using  $\text{LiFePO}_4$  for the positive electrode of a lithium ion battery is proposed in JP,9-171827,A. Volume density is [ cm ] as large as 3.36g /,  $\text{LiFePO}_4$  generates the high potential of 3.4V, and its geometric capacity is also as large as 170mAh/g. And  $\text{LiFePO}_4$  is an initial state, and since it contains electrochemically one Li in which a \*\* dope is possible per Fe atom, it is a material promising as a positive active material of a lithium ion battery. Moreover, this  $\text{LiFePO}_4$  is compoundable by simple technique so that it may mention later.

[0011] However, by the actual cell constituted, using  $\text{LiFePO}_4$  as a positive active material, only 60mAh/g-70mAh/about g actual capacity is obtained as reported by the above-mentioned official report. Then, although 120mAh/about g actual capacity is reported in Journal of the Electrochemical Society, and 144 and 1188 (1997), if it considers that a geometric capacity is 170mAh/g, it cannot be said that it has sufficient capacity.

[0012] Since  $\text{LiMn}_2\text{O}_4$  has the capacity a mean voltage is 3.9V and is [ capacity ] 120mAh/g and 4.2g / of volume density is [ cm ] 3 further when  $\text{LiFePO}_4$  is compared with  $\text{LiMn}_2\text{O}_4$ , as compared with  $\text{LiMn}_2\text{O}_4$ , a voltage and the volume density of  $\text{LiFePO}_4$  will be for example, small about ten percent. For this reason, if it is going to obtain the same capacity of 120mAh/g,  $\text{LiFePO}_4$  will become small twenty percent or more with a volume energy density ten percent or more with a weight energy

density rather than  $\text{LiMn}_2\text{O}_4$ .

[0013] Therefore, although 140mAh/g or the capacity beyond it is demanded in order to realize  $\text{LiMn}_2\text{O}_4$ , equivalent level, or the energy density beyond it by  $\text{LiFePO}_4$ , such high capacity is not realized until now by  $\text{LiFePO}_4$ .

[0014] Moreover,  $\text{LiFePO}_4$  is conventionally compounded by [ of 800 degrees C ] being comparatively heated at an elevated temperature under the reduction environment in the synthetic powder. When synthetic temperature is high, the load which will consume the part energy and is given to a reactor etc. is also large.

[0015] As a source of Fe in a synthetic powder, the salt of divalent iron, such as the phosphoric-acid first iron ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), and iron acetate ( $\text{Fe}_2(\text{CH}_3\text{COO})_4$ ), is used. Since the phosphoric-acid first iron has low reactivity, synthesis at low temperature is difficult for it. Moreover, although iron acetate is possible for synthesis at low temperature, the problem that a sour gas occurs is in a synthetic reaction. As for the influence which it has on the periphery, it is large that this sour gas becomes the cause which damages a reactor etc.

[0016] It aims at offering the synthetic technique of  $\text{LiFePO}_4$  from which  $\text{LiFePO}_4$  which is more compounded at low temperature and has high capacity is obtained, and the manufacture technique of the nonaqueous electrolyte cell using the  $\text{LiFePO}_4$  as a cell active material, without proposing this invention in view of the conventional actual condition which was mentioned above, and generating a sour gas.

[0017]

[Means for Solving the Problem] The synthetic technique of  $\text{LiFePO}_4$  of this invention is faced compounding  $\text{LiFePO}_4$ , and it has the mixed process which mixes two or more matter used as a synthetic powder, and is used as a precursor, and the heating process to which heat the above-mentioned precursor obtained at the above-mentioned mixed process, and it is made to react, and is characterized by using a ferrous oxalate at least as the above-mentioned synthetic powder in the above-mentioned mixed process.

[0018] By the synthetic technique of  $\text{LiFePO}_4$  concerning this invention which was mentioned above, since the ferrous oxalate is used as a synthetic powder, gas which affects the periphery at the time of a reaction does not occur.

[0019] Moreover, the manufacture technique of the nonaqueous electrolyte cell of this invention The positive electrode which has for a lithium  $\text{LiFePO}_4$  in which a dope and a \*\* dope are possible in reversible as a positive active material, The negative electrode which counters with the above-mentioned positive electrode, is allotted, and has for a lithium the negative-electrode active material in which a dope and a \*\* dope are possible in reversible, The mixed process which faces being the manufacture technique of the nonaqueous electrolyte cell equipped with the nonaqueous electrolyte which intervenes between the above-mentioned positive electrode and the above-mentioned negative electrode, and compounding the above  $\text{LiFePO}_4$ , mixes two or more matter used as a synthetic powder, and is used as a precursor, It has the heating process to which heat the above-mentioned precursor obtained at the above-mentioned mixed process, and it is made to react, and is characterized by using a ferrous oxalate at least as the above-mentioned synthetic powder in the above-mentioned mixed process.

[0020] By the manufacture technique of the nonaqueous electrolyte cell concerning this invention which was mentioned above, since it faces compounding  $\text{LiFePO}_4$  and the ferrous oxalate is used as a synthetic powder, gas which affects the periphery at the time of a reaction does not occur. And the nonaqueous electrolyte cell by which this  $\text{LiFePO}_4$  has high capacity since a diffusion of the lithium within grain is fully performed is realized.

[0021]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0022] The example of 1 configuration of the nonaqueous electrolyte cell manufactured with the application of this invention is shown in drawing 1. This nonaqueous electrolyte cell 1 is equipped with the separator 6 allotted between a negative electrode 2, the negative-electrode can 3 which holds a negative electrode 2, the positive electrode 4, the positive-electrode can 5 which holds a positive electrode 4, and a positive electrode 4 and the negative electrode 2, and the insulating gasket 7, and it comes to fill up nonaqueous electrolyte in the negative-electrode can 3 and the positive-electrode can 5.

[0023] A negative electrode 2 consists for example, of a metal lithium foil used as a negative-electrode active material. Moreover, in using the material in which a dope and a \*\* dope of a lithium are possible as a negative-electrode active material, it comes to form the negative-electrode active material layer to which a negative electrode 2 contains the above-mentioned negative-electrode active material on the negative-electrode current collection field. As negative-electrode current collection field, a nickel foil etc. is used, for example.

[0024] As a negative-electrode active material in which a dope and a \*\* dope of a lithium are possible, the conductive polymer and stratified compounds (carbon-material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were doped are used.

[0025] As a binder contained in a negative-electrode active material layer, the well-known resin material usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used.

[0026] The negative-electrode can 3 holds a negative electrode 2, and serves as the external negative electrode of the nonaqueous electrolyte cell 1.

[0027] It comes to form the positive-active-material layer to which a positive electrode 4 contains a positive active material on the positive-electrode current collection field. By this nonaqueous electrolyte cell 1, olivine type  $\text{LiFePO}_4$  compounded by the technique of mentioning later as a positive active material is used. Moreover, as positive-electrode current collection field, an aluminum foil etc. is used, for example.

[0028] As a binder contained in a positive-active-material layer, the well-known resin material usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.

[0029] The positive-electrode can 5 holds a positive electrode 4, and serves as the external positive electrode of the nonaqueous electrolyte cell 1.

[0030] A separator 6 can make a positive electrode 4 and the negative electrode 2 able to estrange, and the well-known material usually used as a separator of this kind of nonaqueous electrolyte cell can be used for it, for example, high polymer films, such as polypropylene, are used. Moreover, the thickness of the relation between a lithium ion conductivity and an energy density to a separator needs the thing thin as much as possible. Specifically, 50 micrometers or less are suitable for the thickness of a separator.

[0031] The insulating gasket 7 is incorporated and united with the negative-electrode can 3. This insulating gasket 7 is for preventing transudation of the nonaqueous electrolyte with which it filled up in the negative-electrode can 3 and the positive-electrode can 5.

[0032] As nonaqueous electrolyte, the solution made to melt an electrolyte in a non-proton nature non-aqueous solvent is used.

[0033] As a non-aqueous solvent, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyrolactone, a sulfoxide, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 2-methyl tetrahydrofuran, the 3-methyl 1, 3-dioxolane, a methyl propionate, a methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used, for example. It is desirable to use chain-like carbonate, such as annular carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, from the point of a voltage stability especially. Moreover, such a non-aqueous solvent may be used independently, two or more kinds may be mixed and one kind may be used for it.

[0034] moreover -- the electrolyte melted in a non-aqueous solvent \*\*\*\*\* --  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3$  -- lithium salt, such as  $\text{SO}_3$  and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , can be used Also of these lithium salt, it is desirable to use  $\text{LiPF}_6$  and  $\text{LiBF}_4$ .

[0035] Below, the manufacture technique of the nonaqueous electrolyte cell 1 which was mentioned above is explained.

[0036] First, olivine type  $\text{LiFePO}_4$  used as a positive active material is compounded. In the gestalt of this operation, a ferrous oxalate is used as an iron source in the synthetic powder of  $\text{LiFePO}_4$ .

[0037] Compared with the phosphoric-acid iron used conventionally, the decomposition temperature of a ferrous oxalate is low as a synthetic powder of  $\text{LiFePO}_4$ . Therefore, the synthetic reaction of  $\text{LiFePO}_4$  can be quickly advanced by using a ferrous oxalate as a synthetic powder. Moreover, since gas which affects it at the time of a reaction and affects the periphery by using a ferrous oxalate as a synthetic powder of  $\text{LiFePO}_4$  at it, such as a sour gas, does not occur, a reactor etc. is not damaged.

[0038] In order to compound  $\text{LiFePO}_4$ , first, as a synthetic powder, a ferrous oxalate ( $\text{FeC}_2\text{O}_4$ ), phosphoric-acid hydrogen ammonium ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), and a lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) are mixed by the predetermined ratio, and it considers as a synthetic precursor. Here, it is necessary to fully perform mixture of a synthetic powder. Since each raw material is mixed uniformly and a point of contact increases by fully mixing a synthetic powder, it is enabled to compound  $\text{LiFePO}_4$  at temperature lower than the former.

[0039] Next,  $\text{LiFePO}_4$  is compounded by heating this synthetic precursor in the inert gas ambient atmosphere, such as nitrogen. At the time of a reaction, a sour gas does not occur and it is not affected to the periphery except that a synthetic reaction progresses quickly, since the ferrous oxalate is used at this time.

[0040] Moreover, as for the synthetic temperature of this  $\text{LiFePO}_4$ , it is desirable to consider as the domain of 350 degrees C or more and 790 degrees C or less.

[0041] Conventionally,  $\text{LiFePO}_4$  was compounded at a comparison-elevated temperature called 800 degrees C. When synthetic temperature was high, the load which will consume the part energy and is given to a reactor etc. was also large.

[0042] As mentioned above, it was enabled to compound  $\text{LiFePO}_4$  also at far low temperature by using a ferrous oxalate as a synthetic powder in case of synthesis of  $\text{LiFePO}_4$  compared with conventional 800 degrees C called 300 degrees C.

[0043] And since  $\text{LiFePO}_4$  could be compounded now also, for example at comparatively low temperature called 300 degrees C, it was enabled to compound  $\text{LiFePO}_4$  by the larger temperature requirement compared with the former, and the width of face of selection of synthetic temperature spread. Then, this invention person examined desirable synthetic temperature paying attention to the relation between the synthetic temperature of  $\text{LiFePO}_4$ , and capacity.

[0044] Consequently, the synthetic temperature of  $\text{LiFePO}_4$  was understood that it is desirable to consider as the temperature of the domain of 350 degrees C or more and 790 degrees C or less. If the synthetic temperature of  $\text{LiFePO}_4$  is lower than 350 degrees C, crystallization cannot fully progress with a chemical reaction and uniform  $\text{LiFePO}_4$  cannot be obtained. Moreover, if the synthetic temperature of  $\text{LiFePO}_4$  is higher than 790 degrees C, crystallization does not advance superfluously, and a diffusion of the lithium within  $\text{LiFePO}_4$  grain does not fully happen, and cannot obtain a capacity high enough. Therefore, by compounding  $\text{LiFePO}_4$  in 350 degrees C or more and 790 degrees C or less, it can be uniform,  $\text{LiFePO}_4$  of a single-phase circuit can be obtained, and high capacity exceeding 120mAh/g of the conventional nonaqueous electrolyte cell can be realized.

[0045] Furthermore, the domains of the more desirable synthetic temperature of  $\text{LiFePO}_4$  are 450 degrees C or more and 700 degrees C or less. The high actual capacity for which 170mAh/g which is  $\text{LiFePO}_4$  geometric capacity is pressed by compounding  $\text{LiFePO}_4$  in 450 degrees C or more and 700 degrees C or less can be obtained.

[0046] As mentioned above, by the technique which was explained,  $\text{LiFePO}_4$  of a single-phase circuit is compoundable at temperature lower than the former by using a ferrous oxalate as a synthetic powder. Moreover, in order to use a ferrous oxalate as a synthetic powder by this technique, there is almost no influence which a sour gas does not generate but it has to the periphery at the time of a synthetic reaction.

[0047] And the nonaqueous electrolyte cell 1 using  $\text{LiFePO}_4$  obtained as mentioned above as a positive active material is manufactured as follows, for example.

[0048] as a negative electrode 2, a negative-electrode active material and a binder are first distributed in a solvent -- making -- the negative electrode of a slurry -- a mixture is prepared next, the obtained negative electrode -- a negative electrode 2 is produced by applying uniformly, drying a mixture on the current collection field, and forming a negative-electrode active material layer the above-mentioned negative electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture Moreover, the metal lithium used as a negative-electrode active material can also be used as a negative electrode 2 as it is.

[0049] as a positive electrode 4,  $\text{LiFePO}_4$  and the binder used as a positive active material are first distributed in a solvent -- making -- the positive electrode of a slurry -- a mixture is prepared next, the obtained positive electrode -- a positive electrode 4 is produced by applying uniformly, drying a mixture on the current collection field, and forming a positive-active-material layer the above-mentioned positive electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture

[0050] Nonaqueous electrolyte is prepared by melting an electrolyte salt into a non-aqueous solvent.  
 [0051] And a negative electrode 2 is held in the negative-electrode can 3, a positive electrode 4 is held in the positive-electrode can 5, and the separator 6 which consists of a porous material layer made from polypropylene etc. between a negative electrode 2 and the positive electrode 4 is allotted. Nonaqueous electrolyte is poured in into the negative-electrode can 3 and the positive-electrode can 5, and the nonaqueous electrolyte cell 1 completes the negative-electrode can 3 and the positive-electrode can 5 by fixing in total through an insulating gasket 7.

[0052] By the manufacture technique of the nonaqueous electrolyte cell 1 which was mentioned above,  $\text{LiFePO}_4$  of a single-phase circuit is compoundable at temperature lower than the former. And the nonaqueous electrolyte cell 1 produced, using this  $\text{LiFePO}_4$  as a positive active material becomes what the dope and \*\* dope of a lithium are performed good, and has a high capacity, and was excellent also in the cycle property.

[0053] In addition, although the method by solid phase reaction of facing compounding  $\text{LiFePO}_4$  in the gestalt of this operation mentioned above, and mixing and heating the powder of the compound used as the synthetic powder of concerned  $\text{LiFePO}_4$  was mentioned as the example and explained, this invention is not limited to this and can apply various chemosynthesis methods other than solid phase reaction.

[0054] In addition, in the synthetic technique of  $\text{LiFePO}_4$  mentioned above, it is desirable to perform [ be / under / concerned precursor / synthetic ] receiving / it ] \*\*\*\*\* processing, and to remove the air contained in the concerned synthetic precursor, before carrying out the heating synthesis of the synthetic precursor.

[0055] If air remains in a synthetic precursor, at the time of synthesis of  $\text{LiFePO}_4$ ,  $\text{Fe}^{2+}$  in the ferrous oxalate which is a divalent iron compound will oxidize by the oxygen in the concerned air, and will turn into  $\text{Fe}^{3+}$ . Consequently, the trivalent iron compound which is an impurity will mix into  $\text{LiFePO}_4$  of a product. Oxidization of  $\text{Fe}^{2+}$  in a ferrous oxalate can be prevented by removing the air contained

in a synthetic precursor by \*\*\*\*\* processing. Consequently, a trivalent iron compound cannot mix into  $\text{LiFePO}_4$  of a product, but  $\text{LiFePO}_4$  of a single-phase circuit can be obtained.

[0056] Moreover, as long as a reaction and crystallization advance by the temperature requirement (350 degrees C or more and 790 degrees C or less) which was mentioned above that what is necessary is just to consider  $\text{LiFePO}_4$  as basic composition as a configuration element of  $\text{LiFePO}_4$ , addition or the part may be replaced for elements other than Li, Fe, P, and O by  $\text{LiFePO}_4$ .

[0057] Moreover, although various raw materials, such as a lithium hydroxide, a lithium nitrate, an acetic-acid lithium, and a phosphoric-acid lithium, can be used as a source of a lithium, in order for gas which affects the periphery not to occur and to compound at low temperature comparatively as a synthetic powder of  $\text{LiFePO}_4$  besides the compound mentioned above, it is desirable to use a reactant high raw material.

[0058] The nonaqueous electrolyte cell 1 concerning the gestalt of this operation which was mentioned above is not limited especially about the configuration, and can make cylindrical, a square shape, a coin type, a button type, etc. a thin shape and the various sizes of a large-sized grade.

[0059] In addition, although the nonaqueous electrolyte cell 1 which used nonaqueous electrolyte was mentioned as the example and the gestalt of operation mentioned above explained it as a nonaqueous electrolyte cell, this invention is not limited to this, and when a solid electrolyte and the solid electrolyte of the shape of gel containing a swelling solvent are used as nonaqueous electrolyte, it can be applied. Moreover, this invention is [ primary cell ] applicable also about a rechargeable battery.

[0060]

[Example] Below, that the effect of this invention should be investigated,  $\text{LiFePO}_4$  is compounded, a cell is produced, using obtained  $\text{LiFePO}_4$  as a positive active material, and the example of an experiment which evaluated the property is described.

[0061] <Example 1>  $\text{LiFePO}_4$  was compounded first.

[0062] In order to have compounded  $\text{LiFePO}_4$ , the phosphoric-acid 2 hydrogen ammonium ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) of the raw material with a large microcrystal size was fully ground beforehand first. Next, after mixing a ferrous-oxalate dihydrate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ), phosphoric-acid 2 hydrogen ammonium ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), and a lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) for 30 minutes with a mortar so that a mole ratio may be set to 2:2:1, the acetone was further made into the solvent and it mixed for 48 hours using the zirconia ball with a diameter of 2mm.

[0063] Next, this mixture was dried until it became clay-like. Then, under the nitrogen draft, by heating with a 120-degree C electric furnace, the remains acetone was removed and the synthetic precursor with very high homogeneity was obtained.

[0064] Next, after performing temporary baking of 300 degrees C and 12 hours under the nitrogen ambient atmosphere to this reaction precursor,  $\text{LiFePO}_4$  was compounded under the nitrogen ambient atmosphere by heating a reaction precursor at 600 degrees C for 24 hours.

[0065] And the cell was produced, using  $\text{LiFePO}_4$  obtained as mentioned above as a positive active material.

[0066] first,  $\text{LiFePO}_4$  dried as a positive active material -- 70 % of the weight and an electric conduction agent \*\*\*\*\* -- acetylene black -- 25 % of the weight and a binder \*\*\*\*\* -- a polyvinylidene fluoride -- 5 % of the weight -- solvent \*\*\*\*\* -- the inside of a dimethylformamide -- uniform -- mixing -- a paste-like positive electrode -- the mixture was prepared In addition, #1300 by the \*\*\*\*\* rich company were used for the above-mentioned polyvinylidene fluoride.

[0067] next, this positive electrode -- the mixture was applied on the aluminum mesh used as the current collection field, under the xerensis argon ambient atmosphere, it dried at 100 degrees C for 1 hour, and the positive-active-material layer was formed

[0068] And the aluminum mesh in which the positive-active-material layer was formed was made into the pellet-like positive electrode by piercing to disc-like [ with a diameter of 15.5mm ]. In addition, the 60mg active material is supported by this one positive electrode.

[0069] Moreover, it considered as the negative electrode by piercing a lithium metallic foil to a positive electrode and abbreviation isomorphism.

[0070] Moreover, nonaqueous electrolyte was prepared by melting  $\text{LiPF}_6$  in the amount mixed solvent of isochores of propylene carbonate and dimethyl carbonate by the concentration of one mol/l.

[0071] The positive electrode obtained as mentioned above was held in the positive-electrode can, the negative electrode was held in the negative-electrode can, and the separator was allotted between the positive electrode and the negative electrode. Nonaqueous electrolyte was poured in into the positive-electrode can and the negative-electrode can, and the 2025 type coin type test cell was produced by fixing a positive-electrode can and a negative-electrode can in total.

[0072]  $\text{LiFePO}_4$  was compounded like the example except having made heating temperature of a <example 2> reaction precursor into 400 degrees C.

[0073]  $\text{LiFePO}_4$  was compounded like the example except having made heating temperature of a <example 3> reaction precursor into 800 degrees C.

[0074] The powder X-ray diffraction pattern was measured about  $\text{LiFePO}_4$  next compounded by the



technique which was mentioned above. The measurement conditions of powder X-ray diffraction are shown below.

[0075] Equipment [ Used ]: Rigaku RINT2500 rotating-target X-ray:CuKalpha, 40kV, a 100mA goniometer:vertical-mold canonical, Radius Counter Monochromator [ of 185mm ]:use VCF:use The slit width:diver \*\*\*\*\* slit (DS) =1 degree \*\*\*\*\* slit (RS) =1 degree scattering slit (SS) =0.15mm coefficient equipment:scintillation counter measuring method:reflection method not to carry out, Continuity Scan Scanning-zone: LiFePO<sub>4</sub> powder X-ray diffraction pattern compounded in the example 1 - the example 3 by 2 theta= 10 degrees - 80 degree scan speed:4 degrees/is shown in drawing 2 . LiFePO<sub>4</sub> of the example 1 - the example 3 understands that presence of impurities other than LiFePO<sub>4</sub> is not checked in a product, but LiFePO<sub>4</sub> of a single-phase circuit is obtained from drawing 2 . Thereby, when the heating temperature of a reaction precursor was changed with 400 degrees C, 600 degrees C, and 800 degrees C, it was checked that LiFePO<sub>4</sub> of a single-phase circuit is obtained at any temperature.

[0076] Moreover, the charge and discharge test was performed about the test cell of an example 1.

[0077] First, it charged, changing from constant-current charge to constant-potential charge, and keeping a voltage at 4.5V, when constant-current charge was performed to the test cell and the cell voltage was set to 4.5V. And charge was terminated when the current became two or less [ 0.01mA //cm ]. Then, it discharges, and electric discharge was terminated when the cell voltage fell to 2.0V. In addition, charge and electric discharge were performed in ordinary temperature (23 degrees C), and 0.12mA /of the current density at this time was set to 2 cm.

[0078] The charge-and-discharge property about the cell of an example 1 is shown in drawing 3 . The cell of an example 1 has flat potential in the 3.4V neighborhood, and drawing 3 shows that it has generated a big reversible charge-and-discharge capacity called 163mAh/g for which 170mAh/g which is a geometric capacity is pressed.

[0079] Moreover, the relation between the number of times of a cycle and charge-and-discharge capacity is shown in drawing 4 about the cell of an example 1. Drawing 4 shows that the cell of an example 1 has the cell property which was very as small as below 0.1% / cycle as for the cycle degradation, and was stabilized.

[0080] Therefore, it turns out that LiFePO<sub>4</sub> of a single-phase circuit is compoundable at temperature lower than the former by using a ferrous oxalate as a raw material. And it turns out that the cell using LiFePO<sub>4</sub> of this single-phase circuit as a positive active material becomes what is excellent in a charge-and-discharge property and a cycle property.

[0081]

[Effect of the Invention] By the synthetic technique of LiFePO<sub>4</sub> of this invention, gas which affects the periphery at the time of a reaction does not occur except that a synthetic reaction progresses quickly, since the ferrous oxalate is used as a raw material.

[0082] And the nonaqueous electrolyte cell which has large capacity is realizable with this invention by using LiFePO<sub>4</sub> obtained, using a ferrous oxalate as a raw material as a positive active material.

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[Translation done.]

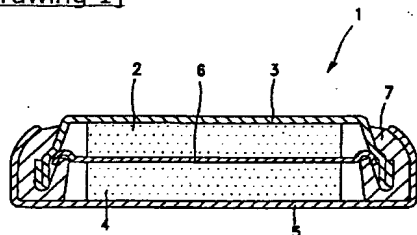
## \* NOTICES \*

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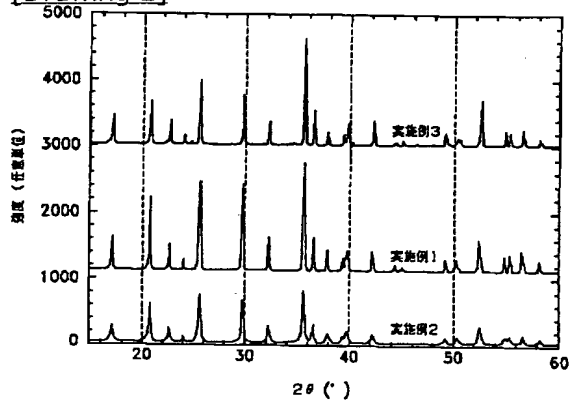
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## DRAWINGS

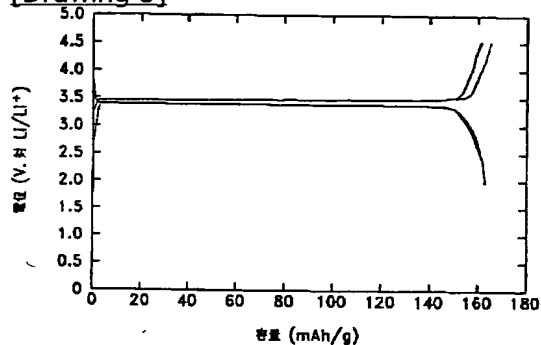
[Drawing 1]



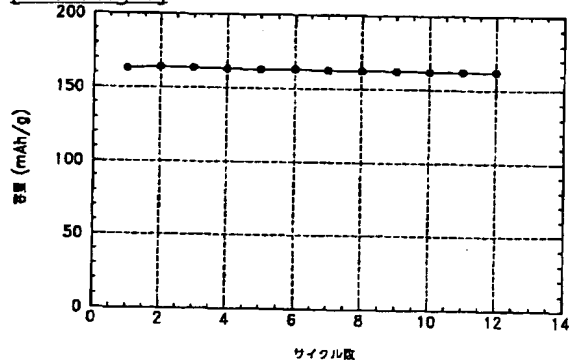
[Drawing 2]



[Drawing 3]



[Drawing 4]



**Improved Iron Based Cathode Material**N. Ravet<sup>a</sup>, J. B. Goodenough<sup>b</sup>, S. Besner<sup>c</sup>,  
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Transition metal-based intercalation compounds are suitable materials for cathode in lithium batteries.

Recently Padhi et al.[1-2] suggested the use of a new compound having the olivine structure:  $\text{LiFePO}_4$ . This iron based compound is environmentally benign and inexpensive. Insertion of lithium occurs reversibly with a very flat discharge plateau at about 3.4 V vs. Lithium.  $\text{LiFePO}_4$  and delithiated  $\text{FePO}_4$  though not intermiscible belong to the same space group with only small change in the unit cell parameters; this makes the material stable upon cycling. Unfortunately the limited accessibility of 0.6 Li atoms per formula unit of  $\text{LiFePO}_4$  found by these authors limits the practical capacity to 100-110  $\text{mAh.g}^{-1}$  capacity, from the theoretical 170  $\text{mAh.g}^{-1}$ .

Here, we report a new route for the synthesis leading to electronically conductive  $\text{LiFePO}_4$  particles with outstanding electrochemical features.

An electronically conductive substance is added during the synthesis, before the formation of crystalline  $\text{LiFePO}_4$ . This substance represents less than 1% by weight of the final product. The crystallographic structure has been confirmed by X-ray.

Electrochemical tests were made at 80 °C, in coin type cells using a polymeric electrolyte.

The improvements of the material are summarized as follows:

- Voltammetric scans performed at 20 mV/h show that the intercalation / deintercalation of lithium is no longer limited (figure 1) and the capacity involved during the discharge process in these conditions is between 94 and 100 % of the theoretical capacity, i.e. 160-170  $\text{mAh.g}^{-1}$ .

- The electronically conductive coating enhances the overall kinetics of the redox reactions. Figure 2 shows potentiostatic scans performed at 170  $\text{mA.g}^{-1}$  corresponding to a charge / discharge rate of C. Once again, the whole capacity is reached.

The addition of a conductive material during the synthesis of  $\text{LiFePO}_4$  improves the practical capacity and the charge / discharge rate. Moreover, the good reversibility of the redox reactions and its predicted low price make  $\text{LiFePO}_4$  an attractive cathode for  $3\text{V}^+$  lithium batteries.

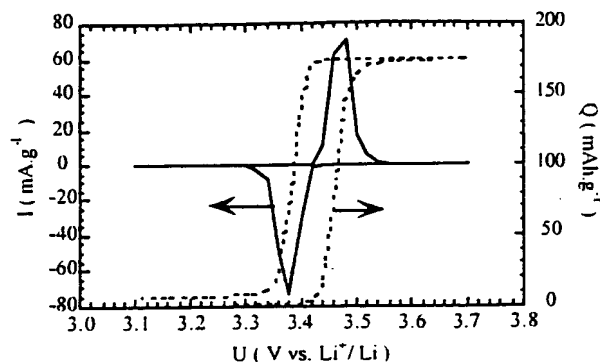


Fig. 1 : Potentiodynamic profiles for  $\text{LiFePO}_4$ . Scan rate 20  $\text{mV.h}^{-1}$ ; temperature 80 °C; electrolyte PEO-Li salt O/Li = 20:1

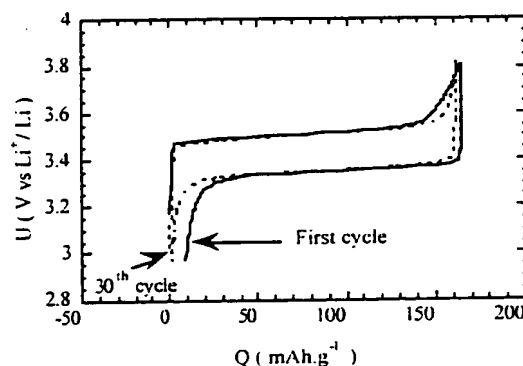


Fig 2 : Charge / Discharge curves of a  $\text{LiFePO}_4$  cathode. Discharge rate C, Temperature 80 °C.

**References:**

1. A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, Proc. 189th ECS Meeting, L.A., May 5-10 (1996).
2. A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 144, 1188 (1997).

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